JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 315–321

Electrode behaviour of insoluble suspensions of metal-free phthalocyanines in methylene chloride

R. O. LOUTFY, J. H. SHARP

Xerox Research Centre of Canada Ltd, 2480 Dunwin Drive, Mississauga, Ontario L5L 1J9, Canada

Received 25 October 1976

A new method of investigating photoactive pigment particles, based on electrochemical measurements on suspended particles in a dielectric fluid containing an indifferent electrolyte is discussed. This technique provides information on the absolute valence and conduction energy levels and band gaps of organic pigments as well as the distribution of states in these solids. The voltammetric oxidations and reductions of the α, β and x-forms of metal-free phthalocyanine (H_2Pc) suspended in methylene chloride were examined on the surface of a hanging mercury drop electrode (HMDE) and a Pt disc electrode (PDE). One of the more significant aspects of the electrochemical studies of these suspensions is that substances of identical chemical composition but different solid state structure, such as α, β and x-H_2Pc, could be examined under the same experimental conditions to give detailed electrochemical information which could be related to the valence and conduction levels.

---

1. Introduction

Most of the work done on the electrode behaviour of suspensions has been mainly concerned with the polarographic reduction of metal halides, metal sulphides, metal oxides, metal selenides, sulphur and insoluble selenium particles [1, 2]. The polarographic properties of carbon suspensions were also investigated [3, 4] recently. However, no work has been carried out on organic solids. It is often difficult to identify the discharge mechanism for the inorganic particle of a suspension. In the absence of dissolution, two mechanisms are usually invoked for polarographic reduction:

(a) Direct electron transfer via interaction of the particle with the electrode;

(b) Indirect reaction involving an intermediate (such as H^+, H atom, molecular oxygen, etc.).

The dropping mercury electrode has been found to be the most suitable electrode for these types of measurements [2], probably because the electrocapillary attachment of solid particles to an electrode surface is possible only when the surface is a liquid, i.e. when it is mobile and capable of sufficient deformation to produce a proper angle of contact at the three phase boundary (electrode – electrolyte – particle) to accommodate the capillarity forces which hold the particle to the electrode surface.

The aim of these studies is to explore the electrochemical behaviour of suspensions of insoluble organic substances such as pigments and polymers in organic liquids. Such systems are classically referred to as colloids when the particle size is between 10^{-7}–10^{-4} cm. The science of colloids is of considerable interest because they are intimately involved in biochemical and physiological processes. The living cell is, in fact, a complex colloidal system. An understanding of the interconnection between the electrochemical aspects of the solid and the free molecule is also an objective of this work.

The phthalocyanine class of compounds is one of the most stable and versatile of organic materials. Phthalocyanines are especially interesting because of their similarity to chlorophyll and hemin. The three known polymorphic forms of metal-free phthalocyanine are the α-, β-, and x modifications which exhibit different optical absorption, electrical and photoconductive properties. For example, Wihksne and Newkirk [5] found that the conductivity of α-CuPc is greater than that of β by a factor of 10^5. On the other hand, Harrison and Ludewig [6] claimed that the difference in conductivity is due to the greater absorptivity for oxygen of the α-phase. This was recently confirmed by Sahai *et al.* [7] who found no significant variation in the electrical properties of the α and β phases of CuPc. However, the origin of photoconductivity and whether it is an intrinsic or extrinsic phenomenon is not settled yet. We have examined the redox properties of the three solid modification of metal-free phthalocyanine in an attempt to get direct information on energy levels, band gaps and the bulk distribution of states which could explain some of the observed differences in the electrical characteristics of these materials.

In this study we employed the HMDE and the PDE which provide an advantage over the DME (dropping mercury electrode) in that the signal fluctuation is much lower.

2. Experimental

2.1. *Apparatus*

A Princeton Applied Research (PAR) Model 174 polarographic analyser, equipped with a PAR Model 9323 hanging mercury drop electrode or a Beckman 2 mm platinum button electrode Model 39281, and a Houston Instrument Model 2000 X–Y recorder were employed for the voltammetric analyses.

The voltammetric cell assembly consisted of a PAR Model 9301 and 9300, cell base and cover, with a hanging mecury drop electrode (HMDE) as cathode and a platinum wire auxiliary electrode as anode. A Brinkmann Model EA410 saturated calomel electrode making contact via a PAR Model 9361 non-aqueous liquid junction bridge served as the reference electrode. For oxidation potential measurements a platinum disc electrode (PDE), 2 mm in diameter, was employed as an anode and a Pt wire as an auxiliary counter electrode.

2.2. *Reagents*

The electrolyte, tetra-*n*-butylammonium perchlorate (TBAP) was obtained from Eastman Kodak. It was polarographic grade and was dried in a vacuum oven at 100° C for 6 h prior to use. Spectral grade methylene chloride, obtained from MC/B, was distilled off P_2O_5 before use. The α- and β-metal-free phthalocyanines were BASF Heliogen blue 7490 and Heliogen blue 7800, respectively; the polymorphic modifications were established using i.r. spectroscopy [14]. The x-H_2Pc was prepared by extensive ball milling of the α-modification [21].

2.3. *Procedure*

Direct current and differential pulse voltammograms were measured on 0.05 mM suspensions of phthalocyanine in 0.1 mM TBAP methylene chloride solution. The hanging mercury drop electrode area was 0·06 cm^2 and the scan rate was 10 mV s^{-1}. The α- and β-H_2Pc powders were suspended in the solvent as received while the x-H_2Pc had to be sonicated in methylene chloride to obtain a fine suspension. Measurements were performed at room temperature (22° C) under a dried argon atmosphere. Photomicrographs of the three polymorphs, showing the particle size and morphology, are shown in Figs. 5 and 6; while the β-H_2Pc micrograph shows definite microcrystallites, those of α- and x-H_2Pc are ill-defined and indicate extensive agglomeration.

3. Results

3.1. *β-Phthalocyanine (BASF)*

The reduction characteristics of β-H_2Pc are similar to those reported for suspensions of inorganic particles [2]. The voltammogram showed a reduction current step over a well-defined potential region (see Fig. 1a), accompanied by sharp current

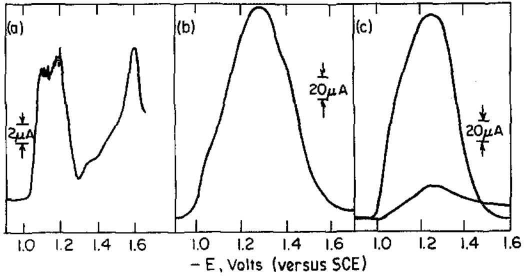

Fig. 1. Reduction voltammogram of suspended (a) β-H_2Pc, and differential pulse voltammetric reduction of suspended (b) α-H_2Pc and (c) x-H_2Pc in CH_2Cl_2 containing 0·1 M TBAP at HMDE.

fluctuations. The potential corresponding to the maximum current is the reduction potential, $E^{red} = -1{\cdot}10$ V (versus SCE). At higher potential, repulsive forces arise and the particles are strongly repelled, and the current falls precipitously. A second reduction peak at a potential of $-1{\cdot}6$ V was also observed.

The magnitude of the peak current is related to the electrode area, the suspension concentration, the frequency of particle impingement, the area and time of contact between the electrode and the suspended particles, and the ohmic resistivity between the particle and electrode [8]. The degree of current fluctuation appears to depend mainly on the particle size and frequency of particle impingement on the electrode. The large current fluctuation observed in the reduction of the β-H_2Pc suspension is attributed to the super-μm dimensions of the β-H_2Pc particles (see Fig. 5b). This phenomenon was not observed in the reduction of either α-H_2Pc or x-H_2Pc where the particle size is of sub-μm dimensions.

The anodic stripping voltammetric technique was also employed and gave a similar result with the oxidation potential of the reduced particles appearing at $-1{\cdot}13$ V (versus SCE). In addition, however, an extra oxidation wave was also observed at about $-0{\cdot}80$ V. This wave is attributed to the catalytic reduction of oxygen by the phthalocyanine.

The voltammetric oxidation at the Pt electrode gave a wave, having an average width of 0·05 V, at $E^{ox} = 1{\cdot}04$ V.

3.2. *α-Phthalocyanine (BASF)*

This material was obtained as a fine powder (sub-μm) and readily formed a well-dispersed suspension in the 0·1 M TBAP methylene chloride solution. The voltammetric reduction of the suspension gave a broad, difficult to resolve, wave centered at $-1{\cdot}28$ V. However, using the differential pulse technique, a well-defined peak at $E^{red} = -1{\cdot}28$ V was recorded which had a width of 0·35 V at half the peak height as shown in Fig. 1b. It should be pointed out that after reduction the α-H_2Pc particles formed a fine coating on the electrode and remained adherent to the electrode surface. This phenomenon is attributed to attractive adhesive forces which become significant when very fine particles are used. For each run, a new Hg drop had to be used.

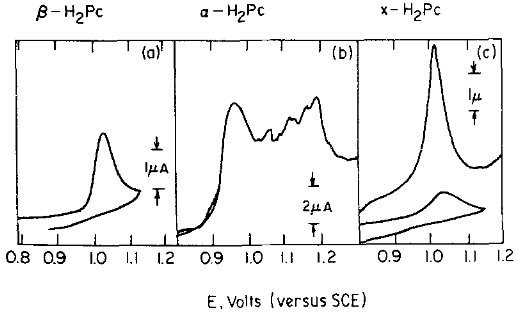

Fig. 2. Voltammetric oxidation of suspended (a) β-H_2Pc, (b) α-H_2Pc and (c) x-H_2Pc in CH_2Cl_2 containing 0·1 M TBAP at PDE.

The voltammetric oxidation of α-H_2Pc in methylene chloride at the Pt electrode exhibited a sharp oxidation wave at $E^{ox} = 0{\cdot}96$ V, as shown in Fig. 2b. The Pt electrode was also found to be coated with α-H_2Pc particles after each run and had to be cleaned and polished prior to reuse. The width of the peak at half peak height was approximately 0·05 V.

3.3. *x-H_2Pc*

The dispersion of x-H_2Pc in the methylene chloride solution was sonicated to form a fine, sub-μm suspension before use. Its reduction waves were similar in character to those of α-H_2Pc, having a reduction potential, $E^{red} = -1.24$ V and a peak width of approximately 0·30 V. The voltammetric oxidation at the Pt electrode occurred at $E^{ox} = 1{\cdot}00$ V (Fig. 2c).

The pertinent electrochemical data for the α, β and x-H_2Pc suspensions are summarized in Table 1.

4. Discussion

The fact that organic solid particles become attached to the electrode surface only in a well-defined region of potential can be ascribed to the disruption of labile layers of electrolyte near the zero charge potential; this is usually termed electrocapillary attachment. Thus, the behaviour of suspensions of insoluble substances at a hanging drop mercury electrode may be described by the following steps:

Table 1. Electrochemical data of insoluble suspensions of metal-free phthalocyanines

Phthalocyanine	$-E^{\mathrm{red}}$ (*V versus SCE*)	*Peak width** (eV)	E_c† (eV)	E^{ox} (V versus SCE)	*Peak width** (eV)	E_v‡ (eV)	E_g§ (eV)	E_g (eV)
(1) β-H_2Pc	1·10 1·04 to 1·18	0·14	3·46	1·04	0·05	5·54	2·08	1·67
(2) x-H_2Pc	1·24 1·06 to 1·36	0·30	3·44	1·00	0·06	5·50	2·06	1·59
(3) α-H_2Pc	1·28 1·15 to 1·50	0·35	3·35	0·96	0·05	5·46	2·11	1·78

* At half-peak height; † Bottom of conduction band, calculated from $E_c = 4{\cdot}5 + E^{\mathrm{red}}$; ‡ Upper edge of valence band, calculated from $E_v = 4{\cdot}5 + E^{\mathrm{ox}}$; § Band gap, $E_g = E_v - E_c$.

(i) Breakdown of the layer of electrolyte adjacent to the electrode as the particle approaches the surface;
(ii) Attachment of the particle to the electrode surface;
(iii) Reduction or oxidation of the solid particle at the electrode.

4.1. *Position of energy levels in organic solids*

A discussion of n-type or p-type conduction mechanisms and boundary-layer problems of organic semi- or photoconductors requires a knowledge of the energetic parameters of the organic solid, as illustrated in Fig. 3. Hitherto, data on the energies of the valence level, E_v, and the conduction level, E_c, (or I_c and EA_c, respectively) are available only for relatively few organic solids. Most of these data are highly dependent on the experimental technique and the surface condition of the sample used. For instance, the exact solid ionization energies, I_c, which are usually obtained from the threshold of photoemission measurements, are rendered difficult to determine by the lack of sharpness in the cutoff of photocurrent versus wavelength plots. The position of the conduction band, obtained from electron beam retardation methods, is often difficult to measure and only approximate values are determined. There is obviously a need for a simple and accurate technique for determining the energetic parameters of organic solids which are of vital importance to understand photovoltaic, contact rectification, and dye sensitization effects. We have found that electrochemical measurements on suspensions of organic semi-conductors is a simple and an informative new technique for this purpose.

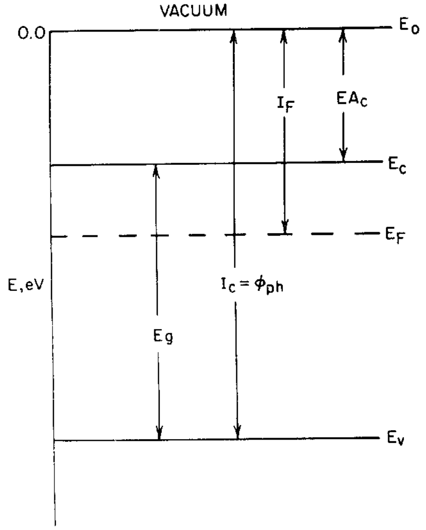

Fig. 3. Energy band scheme for organic solids where E_0, E_c, E_F and E_v are the vacuum, conduction, fermi and valence energy levels, while I_c, EA_c, I_F and E_g represent the solid ionization energy, electron affinity, fermi level and band gap energies.

4.2. *Absolute position of the valence and conduction levels of α, β and x-metal-free phthalocyanines*

Maccoll [9] was the first to point out that the reversible polarographic half wave oxidation ($E^{\mathrm{ox}}_{1/2}$) and reduction potentials ($E^{\mathrm{red}}_{1/2}$) of molecular solutions could be related to the energies of the highest occupied and lowest vacant molecular orbitals respectively, i.e.,

$$E_{\mathrm{HO}} = E^{\mathrm{ox}} + E^0_{\mathrm{RE}} \quad (1)$$

$$E_{\mathrm{IV}} = E^{\mathrm{red}} + E^0_{\mathrm{RE}} \quad (2)$$

where E^0_{RE} is a constant which includes the reference electrode work function.

The oxidation and reduction potentials of the phthalocyanine suspensions were measured against an SCE reference electrode. The free energy of an electron in the reference electrode with respect to vacuum, E^0_{RE}, is 4·50 eV [10]. Using this value for E^0_{RE} and an analogy with the molecular energy levels given in Equations 1 and 2, it is reasonable to construct energy level diagrams for the three phthalocyanine suspensions investigated in this work. In this case, the energies of the valence level, E_V, and the conduction level, E_C, are given by,

$$E_V = E^{ox} + E^0_{RE} \qquad (3)$$

$$E_C = E^{red} + E^0_{RE}. \qquad (4)$$

In the case of reversible one electron redox waves of molecules in solution, the peak widths are generally well-defined and have a width of less than 0·1 V at 25° C. For example, the peak widths of the reduction waves for solutions of lead and manganese phthalocyanine in methylene chloride are 0·08 and 0·05 V, respectively (unpublished observations). In the present work the peak widths of the reduction waves of the metal-free phthalocyanine suspensions were considerably broader, ranging in value from 0·14 to 0·35 V. Although this broadening mechanism is unclear, it is interesting to point out that a similar broadening of energy levels is observed when the absorption spectra of molecules in solution and in the solid state are compared.

The energy level diagrams for the three materials investigated are shown in Fig. 4. The valence and conduction levels of each polymorph were computed from Equations 3 and 4 respectively. Each polymorph has a similar but characteristic set of levels. The valence levels are very narrow (~ 0·05 eV) but the conduction levels are different and considerably broadened (0·14–0·35 eV).

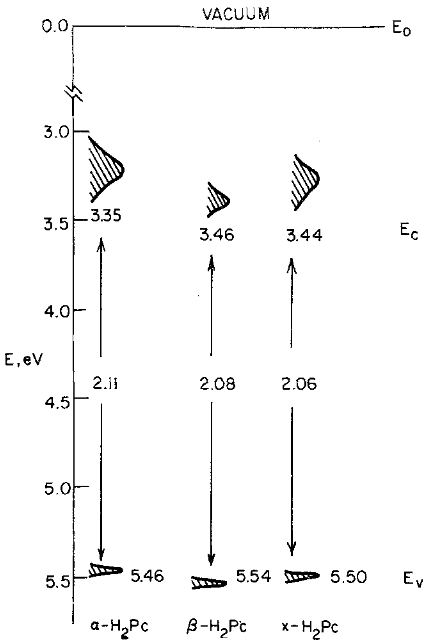

Fig. 4. Energy diagram for α-, β- and x-metal-free phthalocyanines showing the absolute conduction and valence energy levels and the corresponding band gaps.

Perhaps the most reliable photoemission results on metal-free phthalocyanines are those of Schechtman [11] on β-H_2Pc. The E_V value obtained from the photoemission optical densities of states is 5·1 ± 0·2 eV and the E_C value is 3·4 ± 0·3 eV. These are in good agreement with the average values obtained from our electrochemical measurements on H_2Pc suspensions. Other photoemission results are listed in Table 2 for comparison.

Table 2. Comparison of the determined energies of the valence and conduction band of metal-free phthalocyanines

	Kearns and Calvin [15]	Pope [16]	Vilessov [17]	Schechtman [11]	Komp and Fitzsimmon [18]	This work
E_V (eV)	5·15 ± 0·05	5·20 (6·10)	5·10 ± 0·2	5·1 ± 0·2	6·0 ± 0·2	5·4 ± 0·2

	Nelson and Trusty [19]	Vilessov [17]	Meier *et al.* [20]	Schechtman [11]	This work
E_C (eV)	4·3	3·3	3·25	3·4 ± 0·3	3·44 ± 0·2

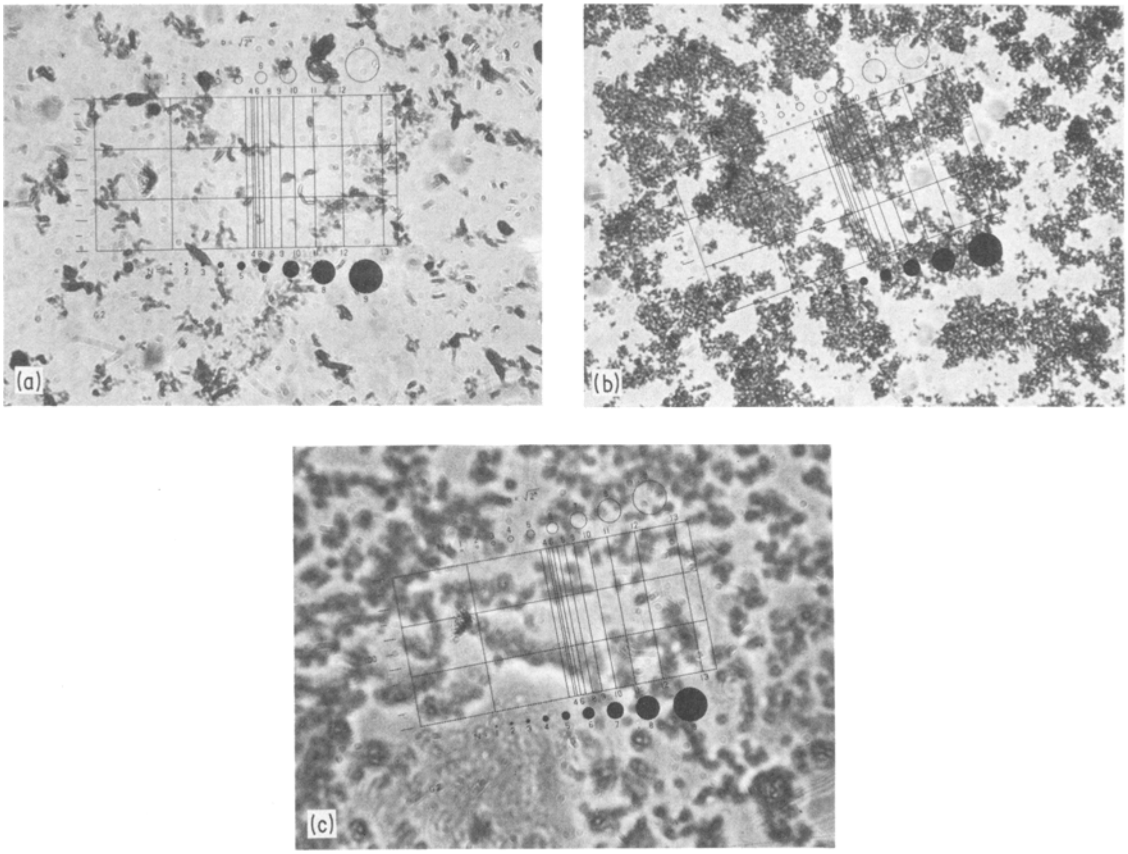

Fig. 5. Optical micrograph of (a) α-H_2Pc, circle 7 = 6 μm; (b) β-H_2Pc, circle 3 = 1·6 μm and (c) x-H_2Pc, circle 6 = 1·8 μm.

4.3. *Energy gap, E_g, of phthalocyanine*

Recently Cox and Knight [12] have shown that at temperatures above 410 K there is good evidence to suggest that the photoconduction process in single crystals of β-H_2Pc is intrinsic, and they measured a thermal activation energy, E', of 0·21 eV, which represents the difference between the bottom of the electron transport band and the singlet exciton level, E_s, at 1·77 eV. Thus $E_s + E' = 1{\cdot}98$ eV. Barbe and Westgate [13] obtained a value of 2·1 eV for E_g from the measurement of the temperature dependence of an ohmic current in a single crystal of β-H_2Pc, which is in excellent agreement with the energy gap of 2·05 eV determined from the electrochemical measurement.

Sharp and Lardon [14] recently reported that the visible lowest singlet excitation energies, E_s, of α;, β- and x-H_2Pc are 1·78, 1·67 and 1·59 eV, respectively. A linear relation between E_g and E_s can be found. It is worth noting that E_s (0–0) is less than the calculated band gap energy by about ~ 0·43 eV in each case. This difference corresponds to the sum of the repulsion and exchange integrals for an excited electron in the free molecule.

In conclusion, this work provides useful information on the intrinsic electrochemical properties of solid organic materials which in turn can be related to the electronic band structure of the solids.

Acknowledgements

The authors wish to thank Drs M. Heyrovsky and K. Micka from the J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovakia, Prague, for their useful comments on our work.

References

[1] M. R. Dausheva and O. A. Songina, *Russ. Chem. Rev.* 42 (1973) 136.

[2] K. Micka, *Adv. Polarography* 3 (1960) 1182.

[3] I. F. Jones and R. C. Kaye, *J. Electroanalyt. Chem.* 20 (1969) 213.

[4] S. V. Hallum and H. V. Drushel, *J. Phys. Chem.* 62 (1958) 110.

[5] K. Wihksne and A. E. Newkirk, *J. Chem. Phys.* 34 (1961) 2184.

[6] S. E. Harrison and K. H. Ludewig, *ibid* 45 (1966) 343.

[7] Y. Sahai, Y. Sadaoha and H. Yakonchi, *Bull. Chem. Soc. Japan* 47 (1974) 1886.

[8] H. D. Hurwitz, S. Srinivasan and M. Litt, *Ber. Bunsenges Phys. Chem.* 75 (1971) 535.

[9] A. Maccoll, *Nature* 163 (1949) 178.

[10] R. O. Loutfy and J. H. Sharp, *Photog. Sci. Eng.* 20 (1976) 165.

[11] B. H. Schechtman, 'Photoemission and Optical Studies of Organic Solids', Stamford University PhD (1969), University Microfilms Inc., *Ann Arbor*, Michigan 69–14, 014.

[12] G. A. Cox and P. C. Knight, *J. Phys. C. Solid State* 7 (1973) 146.

[13] D. F. Barbe and C. R. Westgate, *Solid States* 7 (1969) 563.

[14] J. H. Sharp and M. Lardon, *J. Phys. Chem.* 72 (1968) 3230.

[15] D. R. Kearns and M. Calvin, *ibid* 34 (1961) 2026.

[16] M. Pope, *ibid* 36 (1962) 2810.

[17] F. I. Vilessov, A. A. Zagrubski and D. Z. Garzubov, *Fiz. Tverdogo Tela* 5 (1963) 2000.

[18] R. J. Komp and T. J. Fitzsimmons, 'Electronic Energy States of Certain Sensitizers and Dielectrics', Xerox Research Laboratories, Webster, N. Y. (1968).

[19] R. C. Nelson and J. W. Trusty, *Photog. Sci. Eng.* 16 (1972) 421.

[20] H. Meier, W. Albrecht and U. Tschirwik, *Ber. Bunsenges. Phys. Chem.* 74 (1970) 938.

[21] J. F. Byrne and P. F. Kury, U. S. Patent 3, 357, 989 (1967).